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Damage Resistance and Crystal Growth of KDP*

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Abstract

An investigation is reported of the dependence of laser-damage site density on fluence and on various parameters of crystal growth and post-growth treatment. Damage site density (number of defects per unit volume) was found to increase monotonically with fluence (for single 1-ns pulses of 1.06 μm laser light). Site density (at a fluence of 10 J/cm^2) was influenced by solution flow rate, seed defect removal prior to growth, quaternary ammonium cations, and thermal cycling following growth. No dependence of damage susceptibility on growth rate was found over the range 3-30 mm/d. A model is presented which postulates the electrostatic adsorption of organic material onto the growing crystal surface and subsequent inclusion into the crystal. According to the model, damage occurs by absorption of light by inclusions of solution-wetted organic debris, resulting in pressure increase and hydraulic fracture of the surrounding crystal.

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Introduction

Crystals of potassium dihydrogen phosphate (KDP), widely used for laser beam harmonic generation, undergo an irreversible damage at discrete sites of dimensions 1-15 μm when irradiated with a sufficient intensity of laser light. The damage occurs at fluences of 3-10 J/cm^2 for 1.06 μm laser light at pulse lengths of 1 ns. Despite the interest in improving damage resistance, the cause and the remedy for susceptibility of KDP to laser-induced damage remain to be discovered[1-3]. Earlier researchers at LLNL studied the physical characteristics of damage, but were unable to discover a correlation between damage characteristics and any parameter relevant to crystal growth. They found that damage occurs at discrete sites not necessarily associated with inclusions, scattering sites, voids or crystallographic defects such as dislocation bundles, which could be identified by light scattering or by X-ray topography prior to damage testing. Fluence thresholds for damage increase roughly with the square-root of pulse duration (possibly indicating competing roles of energy absorption and thermal dissipation). Repeated subthreshold pulses improve the resistance of the crystal to damage at higher fluences which would otherwise produce damage. This phenomenon has been called "laser hardening."[2]

Our approach to the study of laser damage phenomena[4] is to test crystals grown as 1 x 2 cm^2 (101) sector blocks under a range of well-defined experimental conditions. From the dependence of damage incidence on experimental parameters (such as solution flow rate, pH, growth rate, etc.) to infer the nature of the damage-causing contamination. Our measure of "damage incidence" is the number of damage sites $n(J_0)$ produced per unit crystal volume after irradiation at a fluence, J_0, by 1-ns, 1.06 μm light.

The variables tested in our survey, summarized in Table 1, were chosen on the basis of plausible damage models. Of these variables, only flow-rate, seed defect refinement, thermal cycling following growth, and quaternary ammonium cations were found to effect changes in damage incidence, n(10), (where n(10) is the number of damage sites per mm^3 produced by a fluence of 10 J/cm^2 in pulses of 1-ns duration). A typical plot of damage incidence as a function of fluence is shown in Figure 1. Damage density increased linearly with solution flow rate over the range 6-100 cm/s, suggesting that the cause of damage was entrapment in the growing crystal of solid particles entrained in the solution flow. The $(CH_3)_4N^+$ ion reduced damage density, suggesting that the particles may contain negatively-charged functional groups which are complexed by the quaternary cation. KDP is expected to possess a positive surface charge during growth, as evidenced by a precipitation potential, due to the small size and high desolvation rates of the potassium ion relative to the larger $H_2PO_4^-$ anion in aqueous complexes. Crystals with small cations and large anions tend to grow with a cation rich surface, or to dissolve with a cation-lean surface. This results in, respectively, a positive or negative surface charge.[5,6]

Seed "defect refinement" (Table 1) refers to the growth from a small seed (5% of the cross-sectional area of the mature crystal seed) from which surface defects had been removed by water etching. Samples grown from such seeds showed a 10-fold reduction in damage incidence at J_0=10 J/cm^2.

While we have identified Bacillus in certain KDP growth solutions, the removal of these bacteria by filtration through 0.2 μm filters had no sensible effect on damage incidence. Most growth experiments were conducted at temperatures above 50 C, where the Bacillus is not viable, and therefore bacterial debris will be scarce. Damage incidence was also independent of growth rate over the range, 3-30 mm/d.

A model consistent with the effects of flow rate, the quaternary cation, and the positively-charged crystal surface postulates the adsorption of pigmented material (such as spores) or partially-carbonized organic material (such as soot, humus or charcoal), and their subsequent incorporation into the crystal to form solution-wetted inclusions. In this model, damage should result from light absorption by the inclusion leading to pressure increase and hydraulic fracture. Partially oxidized carbon or organic matter tends to develop electron-rich carboxylate groups which provide a route to entrapment by the crystal growth by means of adsorption.

Attempts at identifying particulates within the crystal prior to damage by optical means have not been successful. This is possibly a result of the rarity of the sites (in the range of 10^{-9} - 10^{-12} concentration by volume fraction) and the weak attenuation or scattering of light by micrometer-sized inclusions wetted with saturated solution.

We used the model to estimate the absorption characteristics of the debris required for achieving pressures capable of fracturing the crystal. The increase in internal energy of the fluid in a cavity of volume V can be approximated by the equation:

$$\Delta U = J_o \alpha V \tag{1}$$

where J_o is the fluence and α is the absorption coefficient. Equation (1) neglects losses by scattering or conduction to the bulk crystal. We integrate the thermodynamic identity, $dH = dU + PdV + VdP$, with the constraint of constant volume and Eq. (1) to calculate the increase in pressure:

$$P - P_o = \rho(\Delta\hat{H})_p - J_o\alpha \quad . \tag{2}$$

Here P_o is a reference pressure (1 atmosphere) and $(\Delta\hat{H})_p$ is the specific enthalpy interpolated for a fixed density, ρ, from equation-of-state data for water.[4] The dependence of pressure on volume energy increase, $J_o\alpha$, is given in Fig. 2.

The tangential tension σ in a spherical cavity of internal pressure P_i and located within an infinite body is given by $\sigma = P_i/2$. Stress σ for rapid crack propogation depends on defect length b and the fracture toughness constant K_c according to[7] $\sigma_c = K_c/b^{1/2}$. Hence the critical pressure for hydraulic fracture is:

$$P_c = 2\ K_c/b^{1/2} \tag{3}$$

For ADP, $K_c = 2.3\ (10^5)\ \text{Pa-m}^{1/2}$, and b (fracture length) is likely in the range of 0.5- to 5 µm. This range corresponds to a range of critical pressures, 200 - 650 MPa. For damage fluence of 3-10 J/cm^2, the pressure range indicates a range of absorption coefficients of 60- to 400 cm^{-1}. With such low absorption coefficients, organic inclusions of dimensions of 1 micron would absorb only 0.5 to 4% of the incident light and would be difficult to detect with conventional optical microscopy.

These results indicate that voids containing pure KDP solution (having an absorption coefficient of 0.3 cm^{-1}) cannot absorb sufficient energy at 1.06 µm to increase pressure to critical levels. But the absorption by a partially carbonized inclusion could promote damage if the absorption coefficient were in excess of about $10^2\ cm^{-1}$.

The effect of thermal cycling of the crystal (between T_g + 10 C and T_g - 10 C where T_g is the temperature of crystal growth) is consistent with the model. Alternate solution and precipitation of the cavity walls would tend to strengthen the cavity against hydraulic fracture by preferential solution of crystal surface flaws. The same phenomena might also explain laser hardening.

This model indicates possible routes to reducing damage susceptibility:

(1) Spontaneous precipitation of part of the solute from a growth solution should remove trace particulates by adsorption and encapsulation by growing KDP crystallites; subsequent growth from the precipitation-gettered solution should produce a lowered susceptibility to damage. (2) Calcining of the KDP precursors, P_2O_5 and K_2CO_3, at 500 C should combust trace organic material. (3) Direct irradiation of the crystals during growth with intense UV should oxidize trace organics and contaminants. (4) Treatment of growth solution with ozone, electrochemical oxidation by a flow-through porous electrode, or liquid/liquid extraction should remove trace organic contaminants.

Table 1. Parameters investigated in the study of the effect of crystal growth conditions on damage site density.

Parameter	Range	Potential Importance
growth rate	3-35 mm/d	defect generation at high rates
flow rate[a]	6-100 cm/s	transport control
T	50-70 C	kinetic control
pH	3-5	hydrolysis
H_2O_2	1-2%	broad-spectrum oxidation
EDTA	10^{-3}-10^{-4}M	complexes cationic impurities
$(CH_3)_4N^+$ [a]	10^{-2}-10^{-3}M	complexes anionic impurities
bacteria		model of Yokatoni, et al.[3]
filtration	0.2-2 μm	removal of bacteria
continuous UV[b]		effect reported by Yokatoni, et al.[3]
defect refinement [a]		reduces active sites for adsorption
macrostep trajectory		entrapment of particulates between colliding steps
thermal cycling [a]		strengthening of wetted inclusions by preferential solution of flaws
precipitation [b]		gettering of contaminants by precipitation
calcining [b]		removal of trace organics by combustion

[a] changing these parameters had an effect on damage site density.
[b] currently under study.

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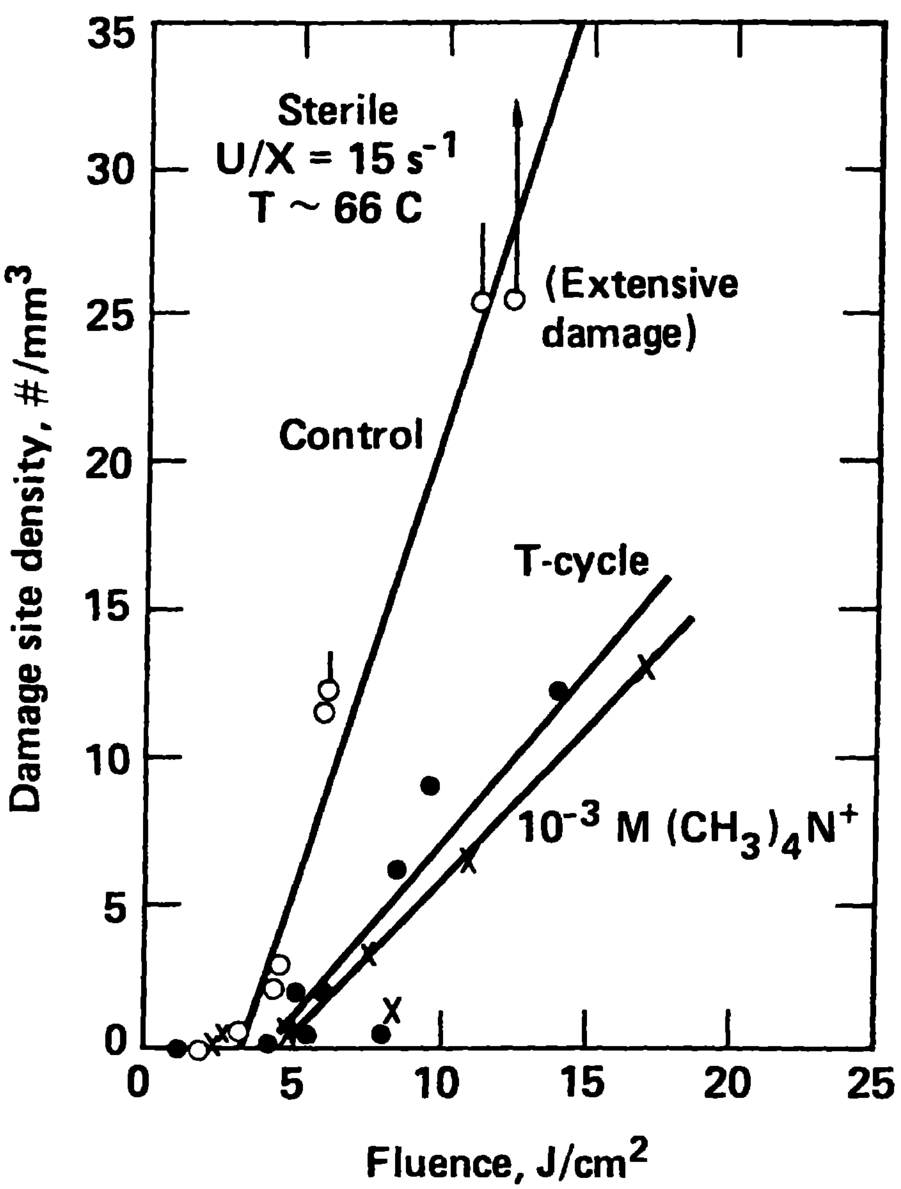
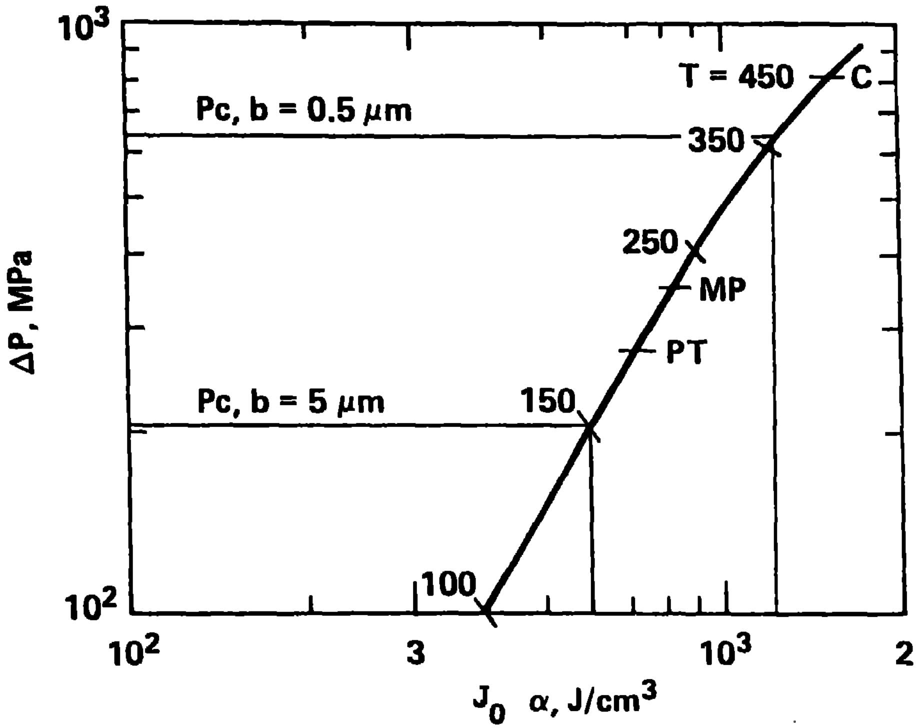
Figure Captions

1. Dependence of damage site density on fluence for crystal growth at $T = 66$ C at rates of 10-20 mm/d, for fixed flow rates. The hydrodynamic parameter, U/X, is the ratio of solution flow rate to length of the growth face in direction of flow. The effects of post-growth thermal cycling and quarternary ammonium cation additions are shown relative to a control sample.

2. The dependence of pressure increase on energy absorption (per unit volume) is derived from the equation of state of water with the constraint of constant volume. Pressures resulting in hydraulic fracture are identified for characteristic crack lengths, $b = 0.5$- and 5 μm. Equilibrium temperatures are given and points of phase transformation (PT) and crystal melting (MP) are indicated.



Sterile
U/X = 15 s-1
T ~ 66 C
(Extensive damage)
Control
T-cycle
10-3 M (CH3)4N+
Damage site density, #/mm3
Fluence, J/cm2
0
5
10
15
20
25
30
35
0
5
10
15
20
25



10^3
10^2
ΔP, MPa
Pc, b = 0.5 μm
Pc, b = 5 μm
T = 450
C
350
250
MP
PT
150
100
10^2
3
10^3
2
J_0 α, J/cm^3